South Coast Air Quality Management District
Science and Technology Advancement

Monitoring and Analysis Division
Laboratory Services Branch

STANDARD OPERATING PROCEDURE

FOR

THE ANALYSIS OF HEXAVALENT CHROMIUM (Cr(VI)) IN AMBIENT AIR BY ION CHROMATOGRAPHY

DRAFT
SOP 0046
Version 3.0
July 26, 2017, 2017

PREPARATION, REVIEWS AND APPROVALS

STANDARD OPERATING PROCEDURE FOR THE ANALYSIS OF HEXAVALENT CHROMIUM (Cr(VI)) IN AMBIENT AIR BY ION CHROMATOGRAPHY

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REVISION HISTORY

STANDARD OPERATING PROCEDURE FOR THE ANALYSIS OF HEXAVALENT CHROMIUM (Cr(VI)) IN AMBIENT AIR BY ION CHROMATOGRAPHY

Version	Date
2.1	March 5, 2010
3.0	July 26, 2017

REVISION CHANGES FROM PREVIOUS VERSION

STANDARD OPERATING PROCEDURE FOR THE ANALYSIS OF HEXAVALENT CHROMIUM (Cr(VI)) IN AMBIENT AIR BY ION CHROMATOGRAPHY

Section	Revisions
All	Comprehensive Revision

TABLE OF CONTENTS

STANDARD OPERATING PROCEDURE FOR THE ANALYSIS OF HEXAVALENT CHROMIUM IN AMBIENT AIR BY ION CHROMATOGRAPHY

TABLE OF CONTENTS (Continued)

Page Number

TABLE OF CONTENTS (Continued)

Page Number

TABLE OF CONTENTS (Continued)

Page Number

DISCLAIMER: Mention of any trade name or commercial product in this Standard Operating Procedure (SOP) does not constitute endorsement or recommendation of this product by the South Coast Air Quality Management District (SCAQMD). Specific brand names and instrument descriptions listed in the SOP are equipment used by the SCAQMD Laboratory. Any functionally equivalent instrumentation, product, or consumable may be used.

1.0 INTRODUCTION

1.1 History

The California Air Resources Board (CARB) identified hexavalent chromium [Cr (VI)] as a toxic air contaminant in January 1986. Chromium is a natural constituent of the earth's crust and is present in several oxidation states. Trivalent chromium [Cr(III)] is naturally occurring, environmentally pervasive and a trace element in man and animals. Hexavalent chromium can originate from a number of commercial and industrial sources. It readily penetrates biological membranes and has been identified as an industrial toxin and cancer-causing substance. Hexavalent chromium is a known inhalation irritant and longer term exposure is linked with respiratory cancer. Exposure often can be associated with emissions from chrome plating and anodizing processes, cement kiln operations, furnaces, and emissions from chromate-treated cooling towers.

Hexavalent chromium has been measured in ambient air at sites located throughout California, including the South Coast Air Basin. Hexavalent chromium is measured by drawing ambient air through sodium bicarbonate impregnated cellulose filters using samplers such as the BGI PQ100 Particulate Samplers (for 47 mm filters) or Xonteck® 924 Toxic Air Samplers (for 37 mm filters). The analysis procedure for hexavalent chromium deposited on 37 mm and 47 mm cellulose filters is described in this document.

1.2 Method Summary

This method is used to determine the amount of Cr(VI) in ambient air by analyzing particulate matter deposited on sodium bicarbonate ($NaHCO_3$) impregnated ashless cellulose filters. The filters are extracted by sonicating in 20 mM sodium bicarbonate solution for one hour. The extract is filtered, then analyzed by ion chromatography consisting of a system comprised of a guard column, analytical column, a post-column derivatization module, and a UV-Vis detector. During the analysis procedure, Cr(VI) exists as chromate due to the near neutral or basic pH of

the eluent. After separation through the column, hexavalent chromium forms a complex with diphenylcarbazide (DPC) forming a chromophore which is detected at a wavelength of 530 nm. The resulting Cr(VI) chromatographic peak retention time and height/area is determined using the Dionex Chromeleon® software. This method is based on a modification of the California Air Resources Board method (Hexavalent Chromium in Ambient Air Method CARB MLD-039 (https://www.arb.ca.gov/aaqm/sop/mld039.pdf).

2.0 INTERFERENCES

2.1 Sodium Carbonate

High levels of sodium carbonate in the sample may cause interferences with the analysis.

2.2 Sodium Bicarbonate

Sodium bicarbonate impregnating solution concentrations in excess of the specified concentration in this method may cause flow restrictions during ambient air sampling.

2.3 Filter Pore Size

Filter pore sizes less than those listed in this SOP have been shown to cause flow restrictions during sampling following sodium bicarbonate impregnation. Sampling details are presented in SOP00052 Standard Operating Procedure for Xonteck® 924.

2.4 Iron, Manganese, Mercury, Molybdenum, Vanadium

These metals may form colored complexes and interfere with the absorbance of hexavalent chromium in the flow cell.

3.0 INSTRUMENT AND EQUIPMENT

3.1 Dionex Ion Chromatographic System Modular Units:

- Gradient or isocratic pump (ICS-3000 DP-1)
- Reagent Delivery Module (ICS-3000 TC-1)
- UV/Vis Detector (ICS Series VWD-1)
- Automated Sampler (AS-1 or AS-AP); controlled directly from the Chromeleon® workstation

This SOP assumes familiarity with the installation and operation of the Chromeleon® software and Dionex ion chromatographic system as specified above. Refer to the Dionex operations manual for detailed instructions in the operation of the Dionex ion chromatograph (IC).

3.2 IC Operating Conditions:

Sample loop volume	1 mL
Analytical column	Dionex IonPac AS7 or equivalent
Guard column	Dionex IonPac AG7 or equivalent
Eluent solution	333 mM Ammonium sulfate ($(NH_4)_2SO_4$) 140 mM Ammonium hydroxide
Eluent flow rate	1.0 mL/min
Post-column reagent	2 mM Diphenylcarbazide (DPC) 10% Methanol 1.8 N Sulfuric acid
Post-column flow rate	0.4 mL/min
Mixing device	750 µL Reaction coil
Detector wavelength	530 nm
Acquisition Software	Dionex Chromeleon®, version 6.8 or greater

3.3 Thermo Scientific Lindberg/Blue M® Vacuum Oven

- Oven temperature: 40° C
- UHP Nitrogen Purge at a flow of ~140 cc/min

4.0 MATERIALS AND CHEMICALS

4.1 Materials

New lots of consumables must be evaluated for contamination prior to use when possible

- 37 mm diameter cellulose filters – 8 µm pore size
- 47 mm diameter cellulose filters – 20 µm pore size
- 37 mm filter ring holders
- 47 mm filter ring holders
- Plastic Petri dishes, large enough to hold a 37 mm or 47 mm filter

- Class A amber volumetric flasks: 1 L and 2 L sizes
- Class A volumetric flasks: 1 L and 2 L sizes
- Amber storage bottles: 1 L sizes
- Wide-mouth Teflon storage jars: 1 L sizes
- Analytical balance
- Pipettor with disposable pipette tips: 100-1,000 µL
- 30 and 50 mL polypropylene centrifuge tubes
- Ultrasonic bath
- Orbital shaker
- Class A graduated cylinders: 25 mL and 100 mL sizes
- Dionex auto-sampler vials (10 mL)
- Filtering apparatus
  - 0.22 µm GSWP filters
  - Filter flask
  - 300 mL filtering glass funnel
  - aluminum clamp
  - glass support base with silicone stopper
  - vacuum pump
- 20 mL disposable syringes
- 0.22 µm hydrophilic polyethersulfone (PES) filters
- Re-pipettor (1 to 10 mL) (bottle top dispenser)
- Lint-free paper towels
- Thermometer
- 4 mm assembly bed supports for guard column

4.2 Chemicals: All chemicals are at least ACS grade**.** All certificates of analysis must be referenced in analysis log book and retained in three ring binder or copied and pasted in log book.

- Ammonium sulfate, 7783-20-2 [$(NH_4)_2SO_4$]

- 1,5-diphenylcarbazide (DPC), 140-22-7 [$C_{13}H_{14}N_4O$]
- Methanol, 67-56-1 [CH_3OH]
- Nitric acid, 7697-37-2 [HNO_3]
- Sulfuric acid, 7664-93-9 [H_2SO_4]

- Sodium bicarbonate, 144-55-8 [$NaHCO_3$]
- Ultrapure sodium bicarbonate, 144-55-8 [$NaHCO_3$]
- Ammonium hydroxide, 1336-21-6 [NH_4OH]
- Nanopure ASTM Type 1 deionized water (>18 MΩ-cm)

4.3 Hexavalent Chromium Stocks

Purchase two stock solutions; one for making working standards at 1,000 ppm, and the other for making a working control at 100 ppm. The two solutions must differ from one another in either lot number or manufacturer and be certified by National Institute of Science and Technology (NIST) or NIST traceable.

5.0 PREPARATION OF SOLUTIONS

5.1 Stock Eluent

To prepare 3 L of stock eluent:

- In a 2 L volumetric flask, dissolve 132 g of $(NH_4)_2SO_4$ in approximately 1,000 mL of deionized water. Dissolve the $(NH_4)_2SO_4$ completely and bring the solution to volume with nanopure water. Filter the solution using the filtering apparatus described in section 4.1.
- In a 1,000 mL volumetric flask, add 28 mL ammonium hydroxide measured using the 100 mL graduated cylinder and bring the mixture to volume with nanopure water.
- Combine the two solutions. The final concentration of stock eluent is 0.333 M ammonium sulfate and 0.140 M ammonium hydroxide.

5.2 Working Eluent

The working eluent is a 1:1 mixture of stock eluent and nanopure water that is mixed by the gradient pump on the instrument. To use the working eluent, first use the

Chromeleon® Panel software to ensure that the eluent pump is off. Transfer the stock eluent to the appropriate reservoir on the IC, then manually open the high-pressure valve on the pump and prime the system for 5 minutes to remove bubbles from the lines using Panel. Close the high pressure valve after priming, then turn the eluent pump on. Investigate obstructions or leaks in the flow path if the eluent pump pressure falls outside of 1,100 – 1,900 PSI.

5.3 Post-Column Reagent

To prepare 1 L of post-column reagent:

- In a 1 L volumetric flask, dissolve 0.5 g of DPC in 100 mL of HPLC grade Methanol.
- When all DPC has dissolved, add roughly 500 mL of nanopure water.
- Place the flask into an ice bath.
- **DO NOT ADD SULFURIC ACID DIRECTLY INTO THE DPC/ METHANOL MIXTURE AS IT WILL REACT VIOLENTLY.**
- Add 50 mL of 96% ACS grade sulfuric acid measured using the 100mL graduated cylinder.
- Slowly bring to volume with nanopure water, allowing time for the solution to cool in order to improve the accuracy of the final volume.
- Filter the solution using the filtering apparatus described in section 4.1.
- Transfer the post-column reagent to the appropriate DPC container for the IC.

The post-column reagent has an expiration date of 48 hours following preparation.

5.4 20 mM Sodium Bicarbonate Extraction Solution

- Dissolve 3.36 g of $NaHCO_3$ in a 2.0 L volumetric flask.
- Bring to volume with nanopure water.
- Filter the solution using the filtering apparatus described in section 4.1.
- Transfer the solution to a clean polyethylene storage container fitted with a calibrated liquid bottle top dispenser.

The sodium bicarbonate solution has an expiration date of 7 days following preparation.

6.0 PREPARATION OF HEXAVALENT CHROMIUM STANDARDS, CHECKS, CONTROLS, AND SPIKE SOLUTION

All hexavalent chromium stocks are to be NIST certified or traceable and are typically acquired in 100 and 1,000 ppm concentrations. Store standards in the refrigerator (LAB 6) at approximately 6^{o} C until ready for use. Prepare calibration, check, control, and spike solutions weekly and store them in the refrigerator. All reagent preparations must be recorded with relevant information in logbook and once prepared on bottle containers. Information must include at a minimum, reagent name, concentrations, date of preparation, expiration date and analyst initials.

6.1 Calibration Standards

Calibration standards are prepared from a 1,000 ppm Cr(VI) stock solution.

6.1.1 Cr(VI) Sub-Stock Solution Preparation

To prepare a 10 ppb sub-stock:

- Dispense 100 µL of 1,000 ppm Cr(VI) stock into a 30-mL centrifuge tube using the 100-1,000 µL pipettor with disposable pipette tips from section 4.1 and then dilute with 9.9 mL of 20 mM $NaHCO_3$ using the bottle top dispenser from section 4.1 to make a 10 ppm Cr(VI) solution.
- Dilute 1,000 µL of 10 ppm Cr(VI) sub-stock to 10 mL in a separate centrifuge tube using 20 mM $NaHCO_3$ from the bottle top dispenser to make a 1 ppm sub-stock solution.
- Dilute 100 µL of 1 ppm Cr(VI) sub-stock to 10 mL in a separate centrifuge tube using 20 mM $NaHCO_3$ from the bottle top dispenser to make a 10 ppb Cr(VI) calibration sub-stock solution.

6.1.2 Calibration Standards

In 30 mL centrifuge tubes, prepare the following working standards with 20 mM NaHCO3:

[Cr(VI)] (ppt)	Volume of 10 ppb Sub-Stock (mL)	Volume of 20 mM $NaHCO_3$ (mL)
50	0.1	19.9
100	0.2	19.8
250	0.5	19.5
500	1	19.0
2,000	4	16.0

6.2 Check Standards/Continuing Calibration Verification (CCV)

The check standard is prepared at 100 ppt from the same 1,000 ppm Cr(VI) parent stock as the calibration standards. Begin by creating a 10 ppb sub-stock solution as described in section 8.1.1 with 20mM $NaHCO_3$ from the bottle top dispenser. Using the 10 ppb sub-stock, dilute the stock down to 100 ppt in a 50 mL centrifuge tube as follows:

[Cr(VI)] (ppt)	Volume of 10 ppb Sub-Stock (mL)	Volume of 20 mM $NaHCO_3$ (mL)
100	0.5	49.5

6.3 Control Standards/Initial Calibration Verification (ICV) and Spike Solution

Control standards are prepared from a secondary 100 ppm Cr(VI) stock; such stock shall be secondary NIST traceable.

6.3.1 100 ppb Cr(VI) Sub-Stock Solution

- Dilute 1,000 µL of 100 ppm Cr(VI) stock to 10 mL in a 30-mL centrifuge tube using 20 mM $NaHCO_3$ from the bottle top dispenser to make a 10 ppm Cr(VI) solution.
- Dilute 100 µL of 10 ppm Cr(VI) sub-stock to 10 mL a 30-mL centrifuge tube using 20mM $NaHCO_3$ from the bottle top dispenser to make a 100 ppb Cr(VI) calibration working stock solution. Prepare the control standards as follows:

[Cr(VI)] (ppt)	Volume of 100 ppb Sub-Stock (mL)	Volume of 20 mM $NaHCO_3$ (mL)
250	0.1 mL	39.9 mL
2,000	1 mL	49 mL

6.3.2 Spike Solution

Dilute 100 µL of 10 ppm Cr(VI) control standard solution with 49.9 mL of 20 mM $NaHCO_3$ from the bottle top dispenser in a 50-mL centrifuge tube to make a 20-ppb spike solution.

6.4 Adding Standards in Element LIMS®

6.4.1 Adding Stock Standards in Element LIMS®

1. From the home screen select "Laboratory" → "Standards"
2. Click "Add"
   a. You will get a prompt
      - Select the type of standard to create:
      - "1. Specify each analyte and its concentration"
      - "2. Combine and/or dilute existing standards"
   b. Select "Specify each analyte and its concentration"
   c. Type in:
      - Description (i.e. Hex Cr Stock Control Standard 100 ppm)
      - Department (Particulates)
      - Expires (expiration date on container)
      - Prepared Date (received date)
      - Prepared By (your name)
      - Vials (1)
      - Volume (i.e. 150 mL)
      - Standard Type → "Other"
      - Reference Date (received date)
      - Solvent/Solvent Lot (i.e. water)
      - Units (i.e. µg/mL)
      - Vendor (i.e. RICCA Chemical Company)
      - Vendor Lot (i.e. 1303934)

- Purchased or Prepared (i.e. Purchased)
- Choose Analytes From: (there is a drop down list of analytes) → select "Hexavalent Chromium" and press "→"
- Hexavalent Chromium will appear under analyte on the right
- Double click the space under µg/mL and enter the concentration (i.e. 100 µg/mL)
- Click "Save"

6.4.2 Adding Control Standards and Spikes in Element LIMS®

Add the following standards in Element LIMS®:

- Hex Cr 20 ppb spike (Lab Control Sample (BS1, BS2))
- Hex Cr 250 ppt Control Standard (Reference Standard (SRM1))
- Hex Cr 2,000 ppt Control Standard (Reference Standard (SRM2))

1. From the home screen select "Laboratory" → "Standards"
2. Click "Add"
   a. You will get a prompt
      - Select the type of standard to create:
      - "1. Specify each analyte and its concentration"
      - "2. Combine and/or dilute existing standards"
   b. Select "Combine and/or dilute existing standards"
   c. Type in:
      - Description (i.e. Hex Cr 20 ppb spike)
      - Department (Particulates)
      - Expires (expiration date is one week from prepared date)
      - Prepared Date (preparation date)
      - Prepared By (your name)
      - Vials (1)
      - Volume (i.e. 500 mL – Note: The volume here will depend on the dilution factor.)
      - Standard Type → "Spike Mix" for spikes, "Reference" for controls
      - Reference Date (prepared date)
      - Solvent/Solvent Lot (i.e. water)
      - Units (i.e. µg/mL)

- Vendor (NA)
- Vendor Lot (-)
- Purchased or Prepared (i.e. Prepared)
- Right click "Standard" → "Browse" → a list of "Particulate Standards" will appear
- Double click the stock standard this solution will be prepared from (Note: Although you will be making serial dilutions, for simplification, the standard will be calculated directly from the stock solution in Element LIMS®. Please adjust dilution factor accordingly.)
- Enter the volume of the stock standard that will be utilized to make the solution (i.e. 0.1 μΛ)
- Click "Save"
- The correct concentration will be calculated under μg/mL

7.0 PREPARATION OF FILTERS FOR HEXAVALENT CHROMIUM SAMPLING

7.1 Documentation Requirements for the Preparation of Filters for Hexavalent Chromium Sampling

All relevant procedures and information for each step of the filter preparation process must be documented in a lab notebook. These steps include:

- Nitric acid washing, pH verification, and drying
- Sodium bicarbonate impregnation and drying
- Final filter acceptance testing
- Light inspection

The lab notebook must include the following information for each filter batch and reagent utilized during this process:

- manufacturer
- lot number
- expiration date

Each set of filters will be assigned a unique identifier based on the filter size and date of the initial preparation. The unique identifier will have the following

format:

2 Digit Filter Size – YYMMDD

Example: a 37 mm filter batch started on January 1, 2014 will have a batch number of 37-140101.

7.2 Preparation of Vacuum Oven

Prepare the ThermoFisher Lindberg Blue M™ Vacuum Oven by wetting a lint-free paper towel with nanopure water and wiping down each surface inside the oven. Remove the stacked trays and Teflon plates from the oven and wipe them down with a nanopure wetted lint-free paper towel. Rinse the trays and Teflon plates with nanopure water and dry them with lint-free paper towels. Store the trays and Teflon plates in the oven until use.

7.3 Preparation of 10% Nitric Acid Wash

Dilute 143 mL of double distilled 70% nitric acid with nanopure DI water in a 1 L volumetric flask.

7.4 Preparation of 0.12 M Sodium Bicarbonate Impregnating Solution

Weigh 10.0 g of sodium bicarbonate in a weighing boat and transfer to a 1 L volumetric flask. Rinse the weighing boat with nanopure DI water into the flask. Add nanopure DI water and swirl the contents until dissolved. Dilute to mark.

7.5 10% Nitric Acid Washing of Filters

Pour freshly prepared 10% nitric acid into a clean wide-mouth 1 L Teflon bottle. Carefully place approximately 200 cellulose filters into the acid solution; be mindful of potential sources of contamination. Place the bottle of filters onto an orbital shaker. Allow the filters to shake at a low speed of (60) for a minimum of 18 hours and a maximum of 24 hours. Rinse the filters thoroughly with DI water until the pH of the rinse solution is 7. Evaluate the pH of three randomly selected filters by placing a pH strip on top of the wet filter; discard the pH strip and filter after use. Continue rinsing the filters if any of the randomly selected filters exceed neutral pH. Once three consecutive filters return a neutral pH, evenly spread the remaining filters on clean Teflon plates and place them inside a ThermoFisher

Lindberg Blue M™ Vacuum Oven at 40° C, purged with UHP nitrogen gas at a flow of roughly 140 cc/min.

7.6 Impregnation of Filters with 0.12 M Sodium Bicarbonate ($NaHCO_3$)

Once the filters dry following the acid washing process, remove them from the oven and soak them overnight on an orbital shaker at low speed (60) in a clean wide-mouth 1 L Teflon bottle filled with 0.12 M $NaHCO_3$ solution. Spread the filters onto clean Teflon plates and place them inside a ThermoFisher Lindberg Blue M™ Vacuum Oven at 40° C purged with UHP nitrogen gas at roughly 140 cc/min until dried.

7.7 Final Filter Acceptance Test

Randomly select 10 filters from the newly impregnated batch. Extract the filters with 10 mL of 20 mM $NaHCO_3$ via sonication in an ice bath for 1 hour. Place the ice away from the samples so as to not block the soundwaves. Filter the solutions and analyze the extracts. The hexavalent chromium values must fall below 20 ppt. Store the batch of filters in the LAB 12 freezer at 0° C or below if all filters meet the acceptance criteria of 20 ppt. If a single filter in the batch exceeds the 20 ppt threshold, then 10 additional filters may be analyzed; all 10 additional filters must pass the acceptance criteria, otherwise the entire batch must be rejected.

7.8 Light Inspection

Inspect the filters for any tears, holes, or discoloration as per OAG QA0044 "Visual Inspection & Acceptance of Filters" following the final acceptance test. Place the accepted filters in a clean plastic bag. Label the bag with the following information:

- Light inspection date
- Type of filter
- Initial of light inspector
- Unique Identifier

Store filters that fail light inspection in a separate bag at room temperature. Label rejected filters with the same information as accepted filters, but clearly identify the batch as rejected. Store the accepted filters in a refrigerator (LAB 12) at approximately 0° C. Freezing minimizes the possibility of the impregnated sodium

bicarbonate reacting with interfering substances present in the air.

8.0 CHAIN OF CUSTODY (COC)

8.1 Pre-sampling

Sodium bicarbonate impregnated filters that meet all criteria from Section 7 are mounted on black or blue rings and placed in labeled plastic Petri dishes for sampling. Perform filter mounting in Petri dishes with great care to avoid contamination. Label each Petri dish with a sample ID (Figure 1) and package it in an individual plastic bag with the chain of custody sheet (COC) (Appendix A) attached to it which specifies the sampling ID, site, and date. Sample COCs are generated through Element LIMS® The filters, in individual petri dishes, can be stored in the freezer until ready for field deployment for up to three weeks.

Figure 1. Labeled and mounted impregnated 37 mm cellulose filter in a Petri dish

8.2 Post-sampling

Filters are received in the laboratory with the sample ID labeled on the plastic Petri dishes and are accompanied by the corresponding COC(s) with the following information:

- retrieval date
- air volume
- average flow rate
- duration of sampling

Any other information relevant to the sample or sampling process must be included as well. Verify that the work order number on the COC corresponds to the received samples and review the COC for accuracy by comparing date, elapsed time, air volume, flow rate, and channel on the COC against the printout from the sampler if it is available.

Inspect the filters for abnormalities. Note any invalid samples. If a filter is found to be invalid, the reason is recorded on the original chain of custody sheet and the sample is assigned a qualifier code in the LIMS system. Store samples in the refrigerator (LAB 15) at approximately 4^{o} C until the samples are extracted. If a problem with the COC is discovered following sample receipt, it is returned to the Senior Chemist who will then contact the Station Operator for clarification and/or corrections to the COC which may result in sample invalidation. A sample could be classified as invalid for the following reasons:

Filter contamination	Filters are either dropped or contaminated by any foreign matter (i.e. dirt, finger marks, ink, liquids)
Damaged or torn	Filters with tears or pinholes which occurred before or during sampling
Flow rate	Average flow rate is less than 9.0 LPM (dependent on sampler)
Flow rate	Average flow rate is greater than 14.0 LPM
Flow rate	Start and stop flow rates differ by more than ±10%
Flow rate	Average flow rate differs from the start or stop flow rates by more than ±10%
Duration	Samplers starting more than ± one hour of specified start time
Duration	Samplers operating ± one hour of specified run time
Power failure	Duration parameters are violated due to a power failure

Sign the COCs for all valid samples and give the original COC to the office assistant so that it may be scanned into Element LIMS®. Place samples in the Lab 15 refrigerator.

8.3 Receiving Samples in Element LIMS®

1. From the home screen select "Sample Control" → "Work Order"
2. Under "Work Order" on the left, select "All" (this will display all samples)
3. Enter the sample number of interest in the space provided (the first 7 digits, i.e. 1403507)
4. Select the "Receipt" tab
    a. Click "Edit"
    b. Change the "Received" date and time and "Received By" to your name
    c. Click "Save"
    d. You will get a prompt "This Work Order is currently at 'Pending' Status. Do you want to update it to 'Received' Status?" → select "Yes"
    e. You will get another prompt "You have changed the Date used for calculation of Analysis Due Dates. This requires updating the Due Dates for all the Samples. Are you sure you want to do this?" → select "Yes"
    f. You will get a third prompt "Work Order Received Date Changed: Change the received date on samples to match?" → select "Yes" and select "Done"
5. Click "Samples" (this will bring you to the list of samples under this work order)
    a. There are 3 tabs in the "Samples" screen: Sample Information, Containers, Qualifiers
    b. Click "Edit"
6. If there is an invalid sample, an appropriate qualifier code must be entered in the Qualifier tab and the reason noted in the "Comments" line in the Sample Information tab. If the sample is valid, then skip this step.
    a. Select the "Qualifier" tab
    b. Double click in the blank space under "Qualifiers"
    c. A list of "Sample Qualifiers" will appear
    d. Each qualifier code will have a corresponding qualifier description
    e. Double click the qualifier of interest (i.e. AH, sample flow rate out of limits)
    f. This will insert a code (i.e. AH) under "Qualifier"
7. Select the "Sample Information" tab
    a. Click on "User-Defined Fields" (a button with a picture of a table next

to the Cross-Table button)
   b. Enter the air volume and click "Apply"
   c. Change the Sample Begin, Sample End, and Sampled By according to the information on the COCs
   d. Enter comments under "Comments" (i.e. invalid, sample flow rate out of limits)
8. Click "Save"

9.0 FILTER EXTRACTION

9.1 Batching Samples for Extraction

Retrieve samples from the freezer with their corresponding COC. Batch the samples in the following manner in the LIMS:

1. From the home screen select "Laboratory" → "Batch"
2. Click "Add"
   a. select "Hexavalent Chromium for IC" in drop down menu located under "Preparation Method"
   b. select "Particulates" in drop down menu located under "Batch Department"
   c. select "Air" in drop down menu located under "Batch Matrix"
   d. under "List Analyses by" make sure "Preparation" is selected and "Hexavalent Chromium for IC" is selected in drop down menu
   e. under "Available" select "Hexavalent Chromium" and press "→" to transfer "Hexavalent Chromium" to "Included" (initial volume must reflect 1 mL and final volume 10 mL for standard filter analysis)
   f. click "Save"
   g. a batch number will automatically be generated
3. click "Bench Sheet"
   a. click "Edit"
   b. click "Add"
   c. select "Client Sample (By Container)"
   d. "All Sample Containers Screen" will appear
   e. select multiple samples of interest by pressing the "Ctrl" key and left

mouse clicking the samples or select single samples by left clicking the mouse twice (this will bypass "f")

f. once the samples have been selected, right mouse click and select "Include Selection"

g. close the "All Sample Containers" screen

4. For QC samples (spikes, blanks, duplicates, reference), click "Add"

a. select QC samples of interest

b. the QC samples will be listed separately from the other samples

- BLK1 (Blank) = 20 mM $NaHCO_3$ and a 47-mm or 37-mm cellulose filter impregnated with $NaHCO_3$. Choose the same size filter as the samples in the batch. If analyzing a batch with 47-mm and 37-mm filters, prepare a filter blank for each filter size.
- BS1 (Lab Control Sample) = 100 µL of 20 ppb Cr(VI) spike solution, 20mM $NaHCO_3$ and a 47-mm or 37-mm cellulose filter impregnated with $NaHCO_3$. Choose the same size filter as the samples in the batch. . If analyzing a batch with 47-mm and 37-mm filters, prepare a blank spike for each filter size.
- ICV1 = 250 ppt Cr(VI) control standard
- ICV2 = 2,000 ppt Cr(VI) control standard

c. If a spike sample is selected, additional information must be added

- right mouse click the spike sample and select "Spike 1 ID"
- "Particulate Spike Mixes" menu will appear
- double click the desired spike solution (Hex Cr 20 ppb spike)
- right mouse click the spike sample and select "Spike 1 Type"
- "QC Sample Properties" will appear
- in drop down menu select "Post-Prep" and press "Apply"
- to add spike amount, right mouse click the spike sample and select "Spike 1 Amount"
- enter the amount (100 µL) in "QC Sample Properties" and press "Apply"
- to add comments, right mouse click the sample(s) of interest and select "Comments" and press "Apply" once the desired comments have been entered

d. If a reference sample is selected, additional information must be added

- right mouse click the spike sample and select "Spike 1 ID"

- "Particulate Spike Mixes" menu will appear
- double click the desired spike solution
- right mouse click the spike sample and select "Spike 1 Type"
- "QC Sample Properties" will appear
- in drop down menu select "Static" and press "Apply"
- to add comments, right mouse click the sample(s) of interest and select "Comments"

e. Click "Save"

f. Click "Done"

9.2 Sample Extraction

Hexavalent chromium concentrations have been shown to decrease significantly with time prior to extraction due to oxidation/reduction and the potential conversion of Cr(VI) to Cr(III) when samples are not kept at low temperatures; as such, sample handling must be kept to a minimum. Samples must be analyzed within 21 days after the sample end date. Sample analysis must be performed within 24 hours of sample extraction, therefore it is important that the IC be equilibrated and ready for analysis once the extraction process is complete. If samples cannot be analyzed within 24 hours, refrigerate sample extracts until analysis is ready to continue.

Batch the samples in Element LIMS®. The maximum number of samples that can be batched are 20 filters (not including blanks and spikes).

Label one polypropylene (30 mL) extraction vessel for each filter number in the batch. Wear gloves to prevent sample contamination. Using clean Teflon tweezers, remove filters from the black/blue ring holders and place them in the labeled extraction tubes. Prepare filter blanks, and filter spikes with each set of extractions. Add 10 mL of 20 mM $NaHCO_3$ in DI water to each sample and cap the tubes tightly with screw caps. Place the rack(s) of polypropylene extraction vessels in a sonicator bath and sonicate for one hour. Add enough ice to the sonicator to prevent the bath from heating the samples during use, and be careful to not add ice onto the top of the caps since it may run into the centrifuge tube during the following step. Confirm that the ice is placed away from the samples so as to not block the soundwaves. Check the sonication process routinely to ensure that the samples do not float in the water as the ice melts. Filter the samples using 20 mL disposable syringes and 0.22

µm PES filters into 10 mL Dionex IC auto sampler vials. Place the vials into the auto sampler. Refrigerate extracts following analysis at approximately 4 ºC until data review is complete.

10.0 FILTER ANALYSIS

10.1 Equipment and Instrument Preparation

10.1.1 Calibration Verification of Variable Volume Pipette

Prior to instrument calibration, verify the calibration of the variable-volume pipette by dispensing 100 µL of water into a weigh boat and placing it on an analytical balance. Record the temperature and measurement from the balance in a lab notebook and repeat this process two more times. Perform this same process at the 1,000 µL level.

Convert the measured masses to volumes using the temperature-adjusted density of water and verify that the average dispensed volumes at 100 and 1,000 µL meet the stated accuracy from the pipette manufacturer. Calculate a relative standard deviation for the dispensed volumes at 100 and 1,000 µL and verify that the values meet the stated precision from the pipette manufacturer.

http://nvlpubs.nist.gov/nistpubs/jres/097/jresv97n3p335_A1b.pdf

10.1.2 Calibration Verification of Variable Volume Bottle top Dispenser

Prior to instrument calibration, verify the calibration of the variable-volume bottle top dispenser by dispensing 5 mL of water into a weigh boat and placing it on an analytical balance. Record the temperature and measurement from the balance in a lab notebook and repeat this process two more times. Perform this same process at the 10 mL level.

Convert the measured masses to volumes using the temperature-adjusted density of water and verify that the average dispensed volumes at 5 and 10 mL meet the stated accuracy from the bottle top dispenser manufacturer. Calculate a relative standard deviation for the dispensed volumes at 5 and 10 mL and verify that the values meet the stated precision from the pipette manufacturer.

10.1.3 Assembly Bed Support Replacement

Assembly bed support replacement must be performed once per week. Ensure that the eluent and post column reagent pumps are off, then remove the guard column from the system. Remove the nut from the inlet side of the guard column and replace the three assembly bed supports found therein. Reassemble the guard column and place it back in line before the analytical column.

10.1.4 Syringe Flushing

Ensure that the autosampler reservoir containing Nanopure DI water is sufficiently filled prior to analysis. Make sure to flush the syringe multiple times following a refill, as failing to do so may introduce bubbles during sample injection.

10.2 Analysis

Analyze an initial blank prior to the IC calibration. The IC is calibrated using the 50 ppt, 100 ppt, 250 ppt, 500 ppt, and 2,000 ppt calibration standards prepared as per Section 6.1. Higher concentration standards can be added to the calibration curve as sample concentrations dictate. Prepare initial calibration verification/initial control standards (250 ppt and 2,000 ppt Cr(VI) solutions) according to Section 6.3 and analyze them immediately following the calibration of the IC. A final initial check standard (100 ppt) and initial calibration blank completes the QC for the calibration. All blanks, checks, and controls must meet the requirements outlined in Table 1 before performing sample analysis. Perform all peak integrations according to SOP 0098 Standard Operating Procedure for Chromatographic Integration.

The average retention times of the 5 calibration standards and the two ICVs must be ±10%. If the difference in retention time exceeds this allowance, check the instrument for problems prior to the analysis of samples. Once all requirements are met, each extracted sample is analyzed with replicate injections taken from the same sample vial, followed by analysis of both a blank and 100 ppt check standard following every ten samples, filter blank or blank spike injections, and after the last injection. These QC solutions must meet the requirements in Table 1, otherwise the samples bracketed by the failed QCs must be reanalyzed. When the Cr(VI) concentration in a sample is above the highest calibration point (2,000 ppt), dilutions must be performed until the sample concentration falls into the calibration range.

11.0 CALCULATIONS

11.1 $\text{Nanograms per Cubic Meter} = \frac{(\text{Average of Replicate Sample (ng/L))} \times \text{Extraction Volume (L))}}{\text{Air volume } (m^3)}$

12.0 QUALITY CONTROL

A quality control summary table (Table 1) is at the end of this section. A flow chart outlining the quality control process is in Appendix C.

12.1 Limit of Detection

The limit of detection (LOD) is a value based on statistical information that is determined annually or after any instrument repair that requires instrument recalibration. The LOD is the lowest concentration of an analyte that the instrument can quantify within a certain confidence level. The calculated limit of detection for the method is determined by analyzing a low standard (e.g. 20 ppt) ten times. The method's calculated limit of detection is determined as follows:

$$LOD = T * SD$$

SD = standard deviation of ten replicate analyses of a standard solution
T = student's T

$T_{0.99} = 2.821$; thus $LOD = 2.821 * SD$

Number of Replicates	***Degrees of Freedom***	***Student's t Value***
7	*6*	*3.143*
8	*7*	*2.998*
9	*8*	*2.896*
10	*9*	*2.821*
11	*10*	*2.764*

12.2 Linearity and Retention Time

Five calibration standards are analyzed with each instrument sequence and are used to produce a linear regression calibration curve. This curve is examined for a

coefficient of determination ≥0.999. If the correlation coefficient is less than 0.999, reanalyze the standards. If the ensuing coefficient of determination is still less than 0.999, re-prepare the calibration standards and reanalyze. In the event that the coefficient of determination continues to fail, investigate the source of the instrument's non-linearity.

The expected retention time is an average of the retention times from the five calibration standards. A sudden or gradual shift in retention time signifies a problem with the instrument. The retention time must be within ± 5 seconds (0.083 minutes) of the expected retention time based on the average retention time of the calibration runs.

12.3 Control Limits

Controls are prepared from a Cr(VI) stock that differs from the stock used to prepare the calibration and check standards. Control standards are analyzed after the calibration is complete and at the end of every sample analysis batch. Control limits are ± 10%. When one or both of the control values are out of the acceptable limits, the instrument is evaluated for problems and appropriate corrective action is taken. Affected samples are reanalyzed until the control is within limits.

12.4 Method Detection Limit (MDL)

Spike at least seven clean filters for each filter size used in the field. Spike using a standard at a concentration three times the estimated detection limit. Extract the spiked filters in accordance with this SOP. The method detection limit must be less than 10 ng/L, which corresponds to an overall limit of detection of 0.006 ng/m^3 for a 17.2 cubic meter ambient air sample extracted in 10 mL of 20 mM $NaHCO_3$ solution. Determine the MDL annually.

12.5 Control Standards/Initial Calibration Verification (ICV)

Control standards (250 ppt and 2,000 ppt) are analyzed after the initial calibration. Control standard limits are ±10% of the target concentration. If one or more control standards are not within limits, affected samples are reanalyzed until all control standards are in range.

12.6 Initial Calibration Blank (ICB)

A 20 mM $NaHCO_3$ solution blank is analyzed before the initial check standards. Values must be below the MDL.

12.7 Filter Blanks

Filter blanks are sodium bicarbonate impregnated cellulose filters. The blanks are extracted and analyzed with each batch of filters. If a batch consists of a mixture of 47-mm and 37-mm cellulose filter samples, both sized filter blanks must be included in the batch. Filter blanks test for any contamination in the 20 mM $NaHCO_3$ extraction solution and in the prepared filters. Filter blanks must be below 20 ppt.

12.8 Laboratory Control Samples (LCS)

Perform spikes using 100 µL of 20 ppb Cr(VI) spiked onto a non-exposed filter. Analyze an LCS with each extracted batch. The LCS must follow the filter blank in the analytical sequence. The calculated filter spike concentration is 200 ppt. Any contamination found in the blank spike must be subtracted from the spiked result. The spike recovery limit is ±10%. If the spike recovery exceeds ±10%, the LCS is reanalyzed. If the spike recovery is still out of the allowable ±10%, the LCS is re-prepared and analyzed. If the previous steps are insufficient, the samples are invalidated and further investigation is performed.

12.9 Check Standards/Continuing Calibration Verification (CCV)

Check standards (100 ppt) are analyzed prior to and after the initial calibration, after every tenth injections of samples, reagent blanks, filter blanks, or blank spikes and at the end of all sample analyses. Check standard limits are ±10% of the target concentration. If one or more check standards are not within limits, samples bracketed by failing QC are reanalyzed until all check standards are in range.

12.10 Replicate Analysis

Every sample is analyzed in replicate. For samples with concentrations greater than lowest point on calibration curve, values must be within 20% of each other. If the values are not within 20%, the sample is reanalyzed.

Table 1. Quality Control Summary Table

Parameter	Frequency	Acceptance Criteria	Corrective Action
Performance Qualification	Annually	LOD - ≤ 20 ppt Linearity - correlation coefficients ≥ 0.999 Blank Test ≤ 20 ppt	1) Check instrument function 2) Perform repair 3) Requalify instrument 4) Submit documentation to QA Branch
Initial Blank	Prior to calibration standards	Below MDL	1) Reanalyze 2) Prepare blank and reanalyze. 3) Correct contamination and reanalyze blank.
Initial 5 point calibration standards	Weekly	Correlation coefficient 0.999 Retention time ±5 seconds from first compared to the last calibration standard	1) Repeat analysis of calibration standards. 2) Re-prepare calibration standards and reanalyze.
Initial Calibration Verification (ICV)/Initial Control Standard	Second source standard, following the initial calibration	Recovery 90-110%	1) Repeat analysis of ICV 2) Repeat analysis of calibration standards 3) Re-prepare calibration standards and reanalyze
Initial Calibration Blank (ICB)	Following the initial check standards	Below MDL	1) Reanalyze 2) Prepare blank and reanalyze. 3) Correct contamination and reanalyze blank.
Filter Blanks	One per extraction batch per filter size	Impregnated filter (<20ppt)	1) Reanalyze 2) Flag data of all samples since the last acceptable blank
Laboratory Control Sample	One per extraction batch per filter size	Recovery 90-110%	1) Reanalyze. 2) Re-prepare spike and reanalyze. 3) Flag data of all samples since the last acceptable spike
Continuing Calibration Verification (CCV)	Every 10 samples and at the end of the analytical sequence	Recovery 90-110% Retention time ±10% from CCV to CCV	1) Reanalyze CCV 2) Reanalyze samples bracketed by failed CCV 3) Re-prepare CCV

Continuing Calibration Blank	After every CCV and at the end of the sequence	Below MDL	1) Reanalyze 2) Prepare blank and reanalyze. 3) Correct contamination and reanalyze blank.
Control Standard	At the end of each batch	Recovery 90-110%	1) Reanalyze. 2) Re-prepare control standards and reanalyze. 3) Flag data of all samples since the last acceptable spike
Replicate Analysis	Every sample	RPD<20% for concentrations greater than or equal to the MRL	1) Check integration 2) Check instrument function 3) Flag samples
Collocated		RPD<20% for concentrations greater than or equal to the MRL	1) Check integration 2) Check instrument function 3) Flag samples

13.0 LIMS - EXPORTING, ENTERING, AND REVIEWING DATA

13.1 Exporting data from Chromeleon® 6.8 to Element LIMS®.

1. Open the Chromeleon® 6.8 program
2. Select analysis date of interest on the left column by a single left mouse click (the right column will display samples analyzed on selected date)
3. Left mouse click the first sample of interest and select the rest of the samples by pressing down the shift key and down arrow key simultaneously until all samples have been selected or left mouse click the "No." button (in between "1" and "Name" on the top left of sample sequence screen
4. Go to "File" and select "Batch Report" from the drop down menu or right mouse click selected samples and select "Batch Report"
   a. uncheck "Printout"
   b. check "Export"
   c. in the "Export Wizard: Common Options" under "Export format(s)" check "ASCII text format (*.txt)
   d. the "Destination" field has the location, directory formula, and file

name formula. These do not need to be changed once they are set unless it is necessary

e. click "Next"
f. select "Integration" from drop down menu
g. select "None" in the Export Raw Data section
h. click "Finish" and "OK"
i. once "Batch Report" export has reached 100% select "OK"

5. For archiving previously analyzed samples, follow instructions below
   a. go to file location: Local Disc C → Documents and Settings → SOUTH COAST AIR QUAL → SOUTH COAST AIR QUAL'S Documents → Chromeleon® → CR6_System → open file with date of interest
   b. change "Sample Name" to Sample ID ELEMENT LIMS® assigns (i.e. 0930911-01)

13.2 Entering and Reviewing Data in Element LIMS®

1. From the home screen select "Laboratory" → "Data Entry/Review"
2. Select "Particulates"
3. Select batch number of interest
4. Select the "Data Entry" tab
   a. click "Create"
   b. click "Datatool" and select samples of interest and click "Done"
   c. click "Merge Files"
   d. click "Done"
   e. click "Save"
5. Select the "Data Review" tab
   a. click "Query"
   b. review final results
   c. right click on data and select "View Details"
   d. review fields in red (fix or add qualifier as necessary)
   e. make changes by selecting "Edit" in "Data Review" tab
6. Highlight all samples to change status
   a. right click in sample area

b. select “Update Status” and click “Update to Analyzed”

7. Highlight all samples to lock samples
   a. right click in sample area
   b. select “Lock”
8. Reviewer Check List
   a. right click in sample area
   b. click “Add a List”
   c. click “Find Checklists”
   d. select “Particulate Analysis Review Checklist”
   e. click “Edit”
   f. click “AutoCheck”
   g. go through the list and make sure all questions are answered
   h. click “Save”

14.0 HAZARDOUS WASTE

14.1 Eluent Disposal

Eluent waste is slightly basic with a pH near 8. The solution can be poured down the drain with water for disposal if needed.

14.2 Hexavalent Chromium Waste

In the laboratory, there are hazardous waste containers for hexavalent chromium working standards. Keep the stock standards in their individual containers. Do not place the stock standards in the working standards hazardous waste container. Contact the Hazardous Waste Coordinator or Chemical Hygiene Officer for the removal of hexavalent chromium stock and working standards.

15.0 MAINTENANCE

15.1 Weekly Maintenance

Prior to calibration, replace the three 4 mm assembly bed supports at the front of the guard column to reduce contamination to the analytical column.

The post-column portion of the system must be cleaned weekly prior to analysis. To do this, first use the Chromeleon® Panel software to ensure that the post-column pump is off, then place a 50/50 water and methanol mixture into the post-column reagent reservoir. Manually open the high-pressure valve on the pump and prime the system for 5 minutes to remove bubbles from the lines using Panel. Close the high pressure valve after priming, then turn the post-column pump on. Leave the post-column pump on for 30 minutes to clean the system. When 30 minutes is up, follow these same pump and prime directions using the post-column reagent prepared in Section 5.3.

15.2 Annual Maintenance

The ICS-3000 is serviced annually by Dionex®. Please refer to the ICS-3000 Ion Chromatography Manual on the Dionex® website for routine maintenance and troubleshooting.

15.3 Additional Maintenance

15.3.1 Pre-Column Cleaning

On a roughly bi-monthly basis, a methanol/water mixture must be run through the pre-column portion of the system in order to keep the lines clean. To do this, remove the column and guard column from the system and directly connect the line leading into the guard column to the line connecting to the post-column T. Ensure that the eluent pump is off in the Chromeleon® Panel software. In this same Panel view, change the reservoir that the eluent pump draws from to the reservoir containing methanol. Open the high pressure valve on the eluent pump and prime the system for 3 to 5 minutes. Turn on the pump motor once the system is primed. The gradient pump will perform a 50/50 mix of the components. Allow the mixture to run through the system for 30 to 120 minutes, then return the Panel parameters to their original state.

15.3.2 Syringe Cleaning

Remove and soak the autosampler syringe needle in methanol for 30 minutes as needed. Allow the needle to dry before placing it back into the autosampler.

16.0 Documentation

16.1 Notebooks/Logbooks

Each instrument has a notebook and a maintenance logbook. They are identified with the instrument name. All notebooks must be kept up to date and written in with blue or black ink. Correct any errors by drawing a single line drawn through the error and it initial and datenext to the correction. Sign and date all notebook pages. For documents taped onto the notebook page(s), initial and dat on so that the initials are half on the notebook page and half on the inserted document.

16.1.1 Instrument Notebook

Notebook inserts are used to record the preparation of all solutions including the working eluent, post-column reagent, and 20mM sodium bicarbonate solution. The notebook insert must have the date of preparation, expiration date if required, the manufacturer and lot number for all reagents and filters used in the preparation. The calibration standards, continuing calibration verification standard, spike solution, and the initial calibration verification standards are included on one notebook insert since they are all prepared at the same time at the beginning of each week.

16.1.2 Maintenance Logbook

All maintenance must be recorded in the instrument maintenance logbook. In addition to weekly and annual maintenance, any errors that occur must also be recorded in the logbook along with the resolution.

APPENDIX A
CHAIN OF CUSTODY

NATTS - EPA
South Coast Air Quality Management District
Special Monitoring Field Sample Log

Cr(VI)

Location: **CELA BLANK** Lab No: **1031307-01**

Sample Begin Date: **11/05/2010 00:00** Date Sample Received: _____

Sample End Date: _____ Reference No: _____

Retrieval Date: _____ Analyst: _____

Filter Load Date: _____

Sample Elapsed Time	Recorded By	Average Flow Rate	Air Volume

Comments:

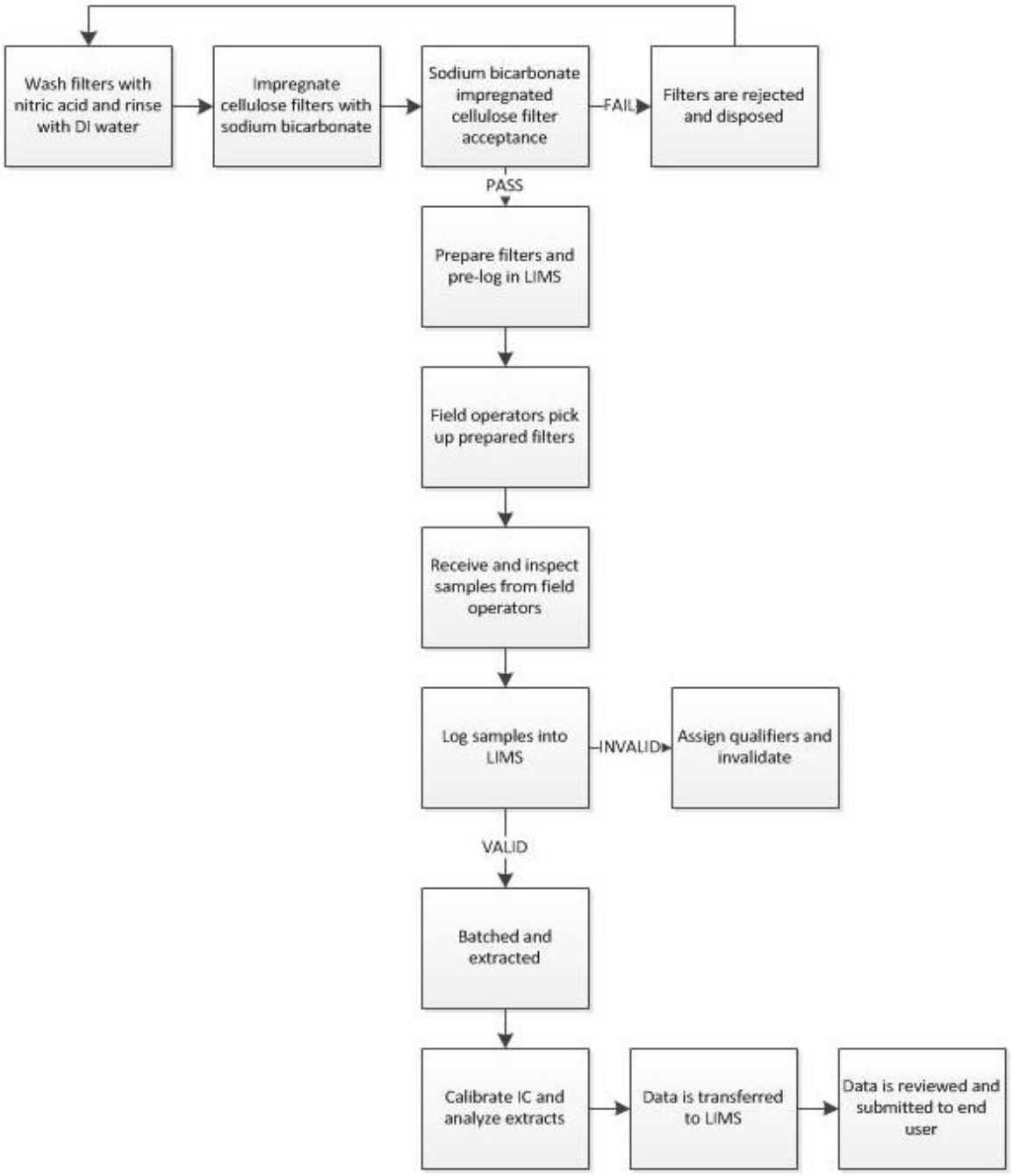
Chain of Custody:

Relinquished By	Received By	Section/Group	Date/Time
Relinquished By	Received By	Section/Group	Date/Time

APPENDIX B
SAMPLE SEQUENCE

Inj.	Sample Name	Ret.Time	Area	Height	Amount	Type	Plates	Dil.Fac.	Comment	Sample ID	Replicate ID
No.		min	mAU*min	mAU	ppt		(EP)				
		CR6	CR6	CR6	CR6	CR6	CR6				
		UV_VIS_1	UV_VIS_1	UV_VIS_1	UV_VIS_1	UV_VIS_1	UV_VIS_1				
1	Blank	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1		System Check	
2	S17E001-ICB1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1		Initial Cal Blank	
3	S17E001-CAL1	7.513	0.0255	0.1341	52.4812	BMB	9926	1	5/1/2017	50 ppt Standard	
4	S17E001-CAL2	7.513	0.0472	0.2521	97.2786	BMB*	10329	1	5/1/2017	100 ppt Standard	
5	S17E001-CAL3	7.513	0.1202	0.6276	247.6587	BMB	10096	1	5/1/2017	250 ppt Standard	
6	S17E001-CAL4	7.507	0.2441	1.2528	502.9303	BMB	10002	1	5/1/2017	500 ppt Standard	
7	S17E001-CAL5	7.507	0.9705	4.9839	1999.6341	BMB*	10021	1	5/1/2017	2000 ppt Standard	
8	S17E001-ICV1	7.507	0.1168	0.605	240.5743	BMB	10040	1	5/1/2017	250 CHECK	
9	S17E001-ICV2	7.507	0.942	4.8371	1940.785	BMB	10021	1	5/1/2017	2000 CHECK	
10	S17E001-IBL1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1		IBL	
11	B17E001-BLK1	7.5	0.0016	0.0117	3.3321	BMB*	18113	1	5/1/2017	47mm	
12	B17E001-BLK1	7.5	0.0018	0.013	3.7261	BMB*	14822	1	5/1/2017	47mm	
13	B17E001-BS1	7.5	0.1017	0.5218	209.6038	BMB	10022	1	5/1/2017	47 mm, 200 ppt spike	
14	B17E001-BS1	7.5	0.102	0.5236	210.1317	BMB	10041	1	5/1/2017	47 mm, 200 ppt spike	
15	1712133-03	7.493	0.2397	1.2421	493.8203	BMB	10023	1	4/28/2017	Sample ID	
16	1712133-03	7.493	0.2397	1.2447	493.9362	BMB	10023	1	4/28/2017	Sample ID	
17	1712133-01	7.493	0.0822	0.4325	169.3437	BMB	10177	1	4/28/2017	Sample ID	
18	1712133-01	7.493	0.0808	0.4302	166.4251	BMB	10235	1	4/28/2017	Sample ID	
19	1712133-02	7.493	0.23	1.1902	473.9804	BMB	9986	1	4/28/2017	Sample ID	
20	1712133-02	7.487	0.2313	1.1936	476.6208	BMB*	9968	1	4/28/2017	Sample ID	
21	S17E001-CCV1	7.493	0.0489	0.2588	100.7579	BMB	10100	1		CCV	
22	S17E001-CCB1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1		CCB	
23	1712133-04	7.493	0.1121	0.5829	230.9077	BMB	10004	1	4/28/2017	Sample ID	
24	1712133-04	7.493	0.1132	0.5828	233.1559	BMB	9967	1	4/28/2017	Sample ID	
25	1712133-05	7.493	0.1663	0.8523	342.5509	BMB	9986	1	4/28/2017	Sample ID	
26	1712133-05	7.493	0.166	0.8551	342.0559	BMB	9967	1	4/28/2017	Sample ID	
27	1712133-06	7.493	0.3047	1.5695	627.7832	BMB	10023	1	4/28/2017	Sample ID	
28	1712133-06	7.487	0.3057	1.5746	629.7858	BMB*	10024	1	4/28/2017	Sample ID	
29	1712133-07	7.493	0.0643	0.3346	132.5529	BMB	9986	1	4/28/2017	Sample ID	
30	1712133-07	7.493	0.0633	0.3321	130.4182	BMB	10080	1	4/28/2017	Sample ID	
31	1712133-08	7.493	0.0553	0.2864	113.9593	BMB	10061	1	4/28/2017	Sample ID	
32	1712133-08	7.493	0.0567	0.2945	116.7885	BMB	9873	1	4/28/2017	Sample ID	
33	S17E001-CCV2	7.493	0.0481	0.2526	99.025	BMB	10138	1		CCV	
34	S17E001-CCB2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1		CCB	

APPENDIX C
FLOW CHART FOR HEXAVALENT CHROMIUM



APPENDIX D
REFERENCES

1. California Air Resources Board Method SOP MLD-039: "Standard Operating Procedure for the Analysis of Hexavalent Chromium in Ambient Air by Ion Chromatography"

2. Dionex Technical Note TN24: Determination of Chromium by Ion Chromatography, Dionex Corporation, July 1991.

3. U.S. Environmental Protection Agency Method SOP 5-03: "Standard Operating Procedure for the Determination of Hexavalent Chromium In Ambient Air analyzed By Ion Chromatography (IC)"

4. U.S. Environmental Protection Agency EPA 821-R-16-006: "Definition and Procedure for the Determination of the Method Detection Limit, Revision 2"

5. SOP00052 Standard Operating Procedure for Xonteck® 920.

6. SOP00102 Standard Operating Procedure for Visual Inspection & Acceptance of Cellulose Fiber Filters.

7. SOP0098 Standard Operating Procedure For Chromatographic Integration